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JOURNAL
OF THE
ELISHA MITCHELL SCIENTIFIC SOCIETY

VOLUME XXX JANUARY, 1915 No. 3

# RECENT CONCEPTIONS OF THE ATOM

BY F. P. VENABLE

The original conception of the atom arose from the discussion among the early Greek thinkers as to the indefinite divisibility or ultimate indivisibility of matter. They were divided into two schools of thought—the plenists and anti-plenists, or vacuists. It was the belief of the latter school that all matter was composed of indivisible particles or atoms, and vacua.

These atoms are not mathematical points but are too small to impress themselves upon the senses and are indivisible. They differ in size, shape and weight; are in continuous motion (hence the necessity for voids); and are endowed with some inclination or force which causes them to meet in a selective way and by their union form the various kinds of matter known to us. This theory was the high achievement of pure reasoning with little basis of experimental evidence. We accept the atoms but for the vacua substitute the very original conception of Aristotle of a *quinta essentia* or ether, of whose existence we still have no tangible proof.

Through the centuries this theory of atoms has come down to us without important change or experimental support until Dalton made use of it to explain the great underlying laws of chemistry and attempted for the first time to determine the relative weights of these ultimate particles or atoms.

Dalton's conception of the atom becomes of greater interest in view of the modern speculations. In his New System of Chemical Philosophy (p. 147) he writes: "A vessel full of any

pure elastic fluid presents to the imagination a picture like one full of small shot. The globules are all of the same size, but the particles of the fluid differ from those of the shot in that they are constituted of an exceedingly small central atom of solid matter, which is surrounded by an atmosphere of heat, of great density next the atoms but gradually growing rarer according to some power of the distance: whereas those of the shot are globules uniformly hard throughout and surrounded with atmospheres of heat of no comparative magnitude."

How stubbornly the notion of the material nature of heat was held to may be realized from an examination of Lavoisier's explanation of the expansion and contraction of matter and from the fact that it was included by some in the list of elements for years after the time of Dalton.

According to Dalton's hypothesis these atoms of definite and distinctive weight combined under certain fundamental laws to form the various substances that make up the material world. As to the size and form, the chemist gave himself no concern, but took up the task of finding out the exact, relative weight of every different atom known to him. These atoms he believed to be unchangeable and thus made possible a mathematical basis for his science.

But the physicist is necessarily concerned with the atom also, and at the same time that Dalton reaffirmed the atomic theory, Young gave his reasons for regarding the atom as a perfect elastic sphere in the place of the conceptions that had grown up of mathematical points, various other geometric forms and rigid particles.

The Daltonian atomic theory was slow of acceptance because of the confusion arising between the divisible ultimate particles of compounds and those which so far as was known were undecomposable. A clear distinction had to be drawn between atom and molecule and this was not easy until many facts had been accumulated. Chemists came to know many different kinds of atoms representing as many different elements. These elements were at first called simple bodies, but to accurately define an

element has proved very difficult and one definition after another has been given up as knowledge has grown.

The atomic theory must stand until a better theory is formulated explaining the laws of combination. This theory in its simple form is independent of speculation as to the nature of the atom. Of course the views as to this nature have greatly changed with the growth of knowledge and the chemist has learned to be cautious in his attempts at definition. It is enough for him to know that the supposedly unchanging atom is at least unchanged by the forces and the conditions with which he works and that he can safely count upon it to act in the future as it has in the past. It cannot be decomposed so far as is known by any means at his command and even if such decomposition were effected the laws of combination would remain the same.

It may not be simple or a unit in itself. In fact, both chemist and physicist have long known multiplied reasons for believing in its complexity, but under the influences of forces that bring about combination and decomposition it behaves as a simple unit. And so, while the study of this complexity is most fascinating, the discovery of the nature and constitution of the atom can make no change in the part it has played in the upbuilding of chemical science.

But this science is deeply concerned with the constitution of matter. It is the prime object of its striving and we can no longer look upon the atom as the ultimate particle. The numerous light waves of different length revealed in the spectra, the intimate relationship shown in the periodic system, and other facts forbid this. We must go deeper, if possible, and find out how the atom itself is built up.

Prout, in 1814, thought of the atom as built up of hydrogen. Graham in 1863, conceived of one ultimate, common atom in different conditions of movement. In 1887, Crookes suggested a hypothetical primal atom, protyle, which, under the influence of electricity, gave rise to the various elemental atoms. These were, of course, speculations without basis of experiment and serve mainly to show the trend of thought. In fact, being be-

yond the range of experimentation, they were unproductive of useful results.

And so the chemist became cautious in his definition of atoms, regarding them as a series of related bodies, complex in nature and hence probably divisible but indivisible by any means known to him, each remaining as a unit under the influence of the ordinary forces which might be applied to them. Each one made itself known as a group of associated properties, or as Patterson-Muir put it: "The name copper is used to distinguish a certain group of properties that we always find associated together from other groups of associated properties, and if we do not find the group of properties connoted by the term copper, we do not find copper."

The discovery by Sir William Ramsay in 1894 of argon, followed in 1898 by that of neon, krypton, xenon and helium, brought a new phase into the discussion. Here were atoms destitute of all power of combination, even with similar atoms, hence existing as monatomic gases and presenting no so-called chemical properties for comparison. They formed a new group in the periodic system and had to be accounted for in some way.

It is interesting to me personally that as sectional chairman, I delivered an address in 1899 before the section of chemistry of the A. A. A. S. in which I spoke as follows: "Is it not fair to assume that argon, helium and their companion gases, having no affinity, are without electrical charge? Were they without affinity from the beginning or did they start out as ordinary atoms and somehow lose this property and with it the power of entering into union of any kind, even of forming molecules? Can these be the changed atoms of some of our well-known elements, a step nearer to the primal elements and with the electrical charge lost? Perhaps the coming century will unfold the answer."

The answer came much sooner than was expected. In 1903, Rutherford and Soddy from the presence of helium in minerals and its inability to enter into combination, suggested that it was probably the product of radio-active changes. Sir William Ramsay had drawn attention to the fact that helium is only

found in minerals which are radio-active, and in the same year, 1903, Ramsay and Soddy established by direct experiment that there is a continuous production of helium from radium. May I not then reaffirm the belief that these monatomic, uncharged gases are all the products of disintegration changes and that the proof will be forthcoming? In fact, the results obtained already by J. J. Thomson, Ramsay, Winchester, Collie, Patterson and Masson, though disputed, and still in doubt, would seem to prove this for neon and argon in addition to the conclusive evidence for helium.

Let us next see something of the relations of the atom to electricity. Dalton's picture of the atom, as we have seen, was that of an exceedingly small central particle of solid matter surrounded by an atmosphere of heat. Davy, in 1807, supposed that these particles were in different electrical states and so accounted for chemical affinity—a theory which was later variously elaborated by Berzelius and others. Faraday's law, according to Helmholtz, tells us that the same definite quantity of either positive or negative electricity moves always with each univalent atom, or with every unit of affinity of a multivalent atom, and accompanies it in all its motions. This quantity we may call the electric charge of the atoms.

In this same Faraday lecture in 1881, Helmholtz added: "The most startling result of Faraday's law is perhaps this. If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions which behave like atoms of electricity."

From the earliest stages of the atomic hypothesis in the efforts at accounting for affinity and valence, phenomena of combination, the vision of the atom became associated with electricity and more or less material conceptions grew up as to this indispensable and equally indivisible accompaniment.

This brings us then to the atom of Sir J. J. Thomson, which, as first stated, was simply made up of corpuscles of negative electricity or electrons. Of course, there are two steps in the evolution of this idea. First, it must be established that nega-

tive electricity consists of particles or corpuscles. The preponderance of evidence seems to be in favor of this view, though it is still rejected by some of the foremost men in electrical science.

The second step is to connect this with the atom. The electro-chemical theory, Faraday's law, complexity of spectra, etc., lend their support, but the strongest confirmation comes from the production of streams of electrons in the disintegration of radio-active atoms.

The electron, according to the calculations of Thomson, has a diameter of $10^{-5}$; that assigned the atom and the mass of the electron would be about one-thousandth that of a hydrogen atom. The original theory of Thomson held that the hydrogen atom with a diameter of $10^{-8}$ cm. was entirely made up of electrons. In the production of an atom the rotating electrons arrange themselves in a number of concentric shells. The number of electrons in such ring and the number of rings necessary to insure the stability of the atom have been calculated. The radiation of energy by the electrons must be small if the atom is to remain stable. The radiation diminishes rapidly with the number of electrons in the ring and with their velocity. With a velocity one-hundreth that of light, the amount of radiation of a symmetrical group of six electrons is one $10^{-16}$ that of a single electron moving with the same velocity in the same orbit. And yet this continuous drain must end either in a rearrangement or in an expulsion of electrons from the atom.

At first the whole mass of the atom was supposed to be made up of electrons and the number of these to be large. Later Thomson showed that the number of electrons was about three times the atomic weight. In such case only a minute fraction of the mass could be made up of electrons.

In summing up the account of the hypothesis, it is sufficient to state, as Rutherford does, that the evidence for the existence of electrons and that these are a universal constituent of atoms is strong, but that the atoms are entirely composed of electrons has little positive evidence for and much against it.

In 1904 (Phil. Mag. [6]-7-237), Thomson states his view that the atoms of the elements consist of a number of negatively

electrified corpuscles enclosed in a sphere of uniform positive electrification, such a model atom having been worked out by Lord Kelvin. This recalls Dalton's atom with its enveloping "sphere of heat."

The Rutherford atom is the last stage in the evolution of the modern conception of this one time indivisible, ultimate particle. This has the advantage over the Thomson atom of an experimental as well as a mathematical basis.

Study of radio-activity phenomena lead Rutherford to announce his Disintegration, or Successive Transformation hypothesis. This has been well worked out and is based upon a large number of observations and experiments. As Rutherford says: "The processes occurring in the radio-active elements are of a character quite distinct from any previously observed in chemistry."

"One of the most powerful methods of obtaining information on the internal structure of the atom," writes Rutherford, "lies in the scattering of high speed particles, for example, of $\alpha$ and $\beta$ particles, in their passage through matter. In consequence of this great energy of motion, a high-speed $\alpha$ or $\beta$ particle must pass through the atom which lies in its path. The deflection of the charged particle from its rectilinear path as the result of an atomic encounter throws light on the intensity and distribution of the electrical forces within the atom to which these deflections are due. One of the most noticeable features of the scattering of $\alpha$ particles by thin films of matter is that a small fraction of the $\alpha$ particles is deflected through angles of more than 90°. If, for instance, the $\alpha$ particles are allowed to strike upon a thin film of gold, some 8,000 pass through, as may be seen by the scintillations given on a zinc sulphide screen. These suffer a certain amount of deflection or scattering, but one is so much deflected as to return to its source."

There appears to be no doubt that the large deflection sometimes suffered by an $\alpha$ particle is the result of a close encounter with only one atom of matter. The type of atom devised by Kelvin and Thomson, says Rutherford, in which the positive electricity is distributed throughout a sphere of radius com-

parable with the diameter of the atom, does not seem capable, without modification, of producing the large deviations of an $\alpha$ particle which are observed.

"The single large scattering of $\alpha$ particles, however, could be explained by supposing that the atom consisted of a concentrated positive charge at its centre and surrounded by a distribution of electrons to render it electrically neutral. It was necessary to suppose that the greater part of the mass of the atom was associated with the positive charge which for distances up to $3 \times 10^{-12}$ cm. behaved as if it were concentrated at a point.

"The large angle scattering of the $\alpha$ particles is then almost entirely due to the passage of the $\alpha$ particle through the intense electric field surrounding the central charge. Supposing the electrical force to vary as the inverse square of the distance from the central charge, the positively charged $\alpha$ particle, in passing close to the centre of the atom describes a hyperbolic orbit, the angle of deflection being greater the nearer the $\alpha$ particle passes the centre of the atom."

The laws of scattering to be expected on this hypothesis have been worked out and verified experimentally. The angle of deflection has been found to depend upon the atomic weight and from examination of the metals from gold to aluminum the positive charge of the nucleus was deduced as $\frac{1}{2}$ Ae.

If the $\alpha$ particles are allowed to bombard the light atoms of hydrogen the smaller nucleus of the hydrogen atom will be projected and this has been proved by experiment. The hydrogen nuclei produce scintillations at a range four times as great as that of the $\alpha$ particles. As calculated by G. C. Darwin, the $\alpha$ particle or helium nucleus must have approached the hydrogen nucleus so that their centres were not more than $1.7 \times 10^{-13}$ cm. distant from one another. The hydrogen atom is taken as composed of one unit charge of negative. electrons and one unit charge of positive electrons.

The Rutherford atom then is made up of a nuclear mass associated with positive electrons (1 unit charge to 2 units mass form a central nucleus which is .0001 of the diameter of the atom). A number of negative electrons in value equal to the

positive nuclear charge circulate around this as an outer shell. The magnitude of the nuclear positive charge in terms of the hydrogen ion charge is probably the same as the atomic number or number of place occupied by the element in the periodic table.

Such an atom as that of Rutherford is, as Soddy observes, not stable according to ordinary electro-dynamical laws since there is nothing to prevent the dispersion of the extremely concentrated central positive charge but, he adds, it is now recognized that these laws require modifications. The model has been used with very considerable success in conjunction with Planck's theory of quanta and leads to results in connection, for example, with the series relationships of the hydrogen and helium spectra in striking accord with experimental determinations.

# A LIST OF PLANTS GROWING SPONTANEOUSLY IN HENDERSON COUNTY, N. C.

BY EDWARD READ MEMMINGER

The following list summarizes the results of years of study of the Flora of Henderson County, but being the work of but one collector is necessarily incomplete. I have entered herein only plants which I have myself seen. Specimens of most of the plants listed are in my private collection and many in Columbia University, N. Y., herbarium.

Henderson County is situated in the western Alpine section of the State; most of the county lying west of the Blue Ridge, and includes in its boundary all sorts of topographic conformations, from the level meadow lands of the French Broad River and its tributaries to mountains of 3,000—4,000 feet in altitude. Most of the level lands of the county are at an elevation of 2,000 feet above sea level. From its altitude its flora approaches greatly the flora of more northern latitudes, so much so that Gray's Flora of the Northern U. S. is nearly of as much use in the study of this flora as Chapman's Southern Flora.

Though this list adds but few new species to the Flora of the State as heretofore published by Curtis and Hyams, yet it extends the ranges of many plants beyond the limits set forth in those lists, and so tends to give us a more accurate knowledge of the distribution of the plants of the State.

The question of nomenclature being in such an unsettled state I have generally adhered to that of Britton and Brown's Illustrated Flora of the Northern States and Canada rather than to the new, radical nomenclature of Dr. Small's Southern Flora.

As the Graminae and Cyperaceae have not been duly studied many species that grow in this country are wanting from this list.

I desire herein to acknowledge the assistance kindly given me in the identification of many species by Dr. Small, Mr. W. W. Ashe and Mr. Biddle of the Biltmore Herbarium.

The list follows:

## PTERIDOPHYTES

*Polypodiaceae*

Polypodium vulgare L.
Phegopteris hexagonoptera (Michx.) Fee.
Pteris aquilina L.
Pteris aquilina caudata (L.) Hook.
Adiantum pedatum L.
Woodwardia areolata (L.) Moore.
Camptosorus rhizophyllus (L.) Link.
Asplenium Trichomanes L.
Asplenium Felix-femina (L.) Bernh.
Asplenium platyneuron (L.) Oakes.
Asplenium acrostichoides Sw.
Dryopteris acrostichoides (Michx.) Kuntze.
Dryopteris noveboracensis (L.) A. Gray.
Dryopteris marginalis (L.) A. Gray.
Dicksonia punctilobula (Michx.) A. Gray.
Onoclea sensibilis L.
Lygodium palmatum (Bernh.) Sw.
Osmunda regalis L.
Osmunda cinnamomea L.

*Ophioglossaceae*

Botrychium ternatum (Thunb.) Sw.
Botrychium virginianum (L.) Sw.

*Lycopodiaceae*

Lycopodium lucidulum Michx.
Lycopodium obscurum L.
Lycopodium complanatum L.

## GYMNOSPERMS

*Coniferae*

Pinus virginiana Mill.
Pinus echinata Mill.
Pinus rigida Mill.
Pinus strobus L.

Abies Fraseri (Pursh) Lindl.
Tsuga canadensis (L.) Carr.
Tsuga caroliniana Engelm. Found only east of the Blue Ridge.
Juniperus virginiana L.

MONOCOTYLEDONS

*Typhaceae*

Typha latifolia L.
Sparganium americanum Nutt.

*Alismaceae*

Sagittaria latifolia pubescens (Muhl.) Smith.
Sagittaria graminea Michx.

*Graminae*

Syntherisma sanguinalis (L.) Nash.
Panicum capillare L.
Panicum viscidum Ell.
Panicum clandestinum L.
Ixophorus glaucus (L.) Nash.
Homalocenchrus oryzoides (L.) Poll.
Andropogon scoparius Michx.
Andropogon virginicus L.
Andropogon glomeratus (Walt.) B. S. P.
Sorghum nutans Gray.
Anthoxanthum odoratum L.
Agrostis alba L.
Agrostis perennans (Walt.) Tuck.
Stipa avenacea L.
Deschampsia flexuosa (L.) Trin.
Trisetum pennsylvanicum (L.) Beauv.
Holcus lanatus L.
Gymnopogon ambigua (Michx.) B. S. P.
Festuca nutans Willd.
Poa pratensis L.
Eragrostis secundiflora Presl.
Uniola laxa (L.) B. S. P.
Elymus canadensis L.

*Cyperaceae*

Scirpus cyperinus Eriophorum (Michx.) Britt.
Eriophorum virginicum L.
Carex crinita Lam.
Carex straminea mirabilis Tuck.
Carex vulpinoidea Michx.
Carex lurida Wahl.
Carex folliculata L.
Carex stricta Lam.
Carex laxiflora patuliflora (Dewey) Carey.

*Araceae*

Arisaema triphyllum (L.) Torr.
Arisaema quinatum (Nutt.) Schott.
Peltandra virginica (L.) Kunth.
Orontium aquaticum L.

*Eriocaulaceae*

Eriocaulon decangulare L.

*Commelinaceae*

Tradescantia virginiana L.
Tradescantia montana Shuttlw.
Commelina virginica L.

*Pontederiaceae*

Pontederia cordata L.

*Juncaceae*

Juncoidea campestris (L.) Kuntze.
Juncus effusis L.

*Liliaceae*

Tofieldia glutinosa (Michx.) Pers.
Chamaelirium luteum (L.) A. Gray.
Stenanthium gramineum (Ker.) Morong.
Melanthium virginicum L.
Melanthium latifolium Desr.
Uvularia perfoliata L.
Uvularia sessilifolia L.
Uvularia puberula Michx.

Chrosperma muscaetoxicum (Walt.) Kuntze.
Lilium carolinianum Michx.
Lilium canadense L.
Lilium superbum L.
Aletris farinosa L.
Erythronium americanum Ker.
Trillium erectum L.
Trillium grandiflorum (Michx.) Salisb.
Trillium stylosum Nutt.
Trillium cernuum L.
Medeola virginiana L.
Polygonatum biflorum (Walt.) Ell.
Polygonatum commutatum (R. & S.) Dietr.
Disporum lanuginosum (Michx.) Nichols.
Vagnera racemosa (L.) Morong.
Convallaria majalis L.
Clintonia umbellulata (Michx.) Torr.
Smilax ecirrhata (Engelm.) Wats.
Smilax glauca Walt.

*Dioscoreaceae*

Dioscorea villosa L.

*Amaryllidaceae*

Hypoxis hirsuta (L.) Coville.

*Iridaceae*

Iris versicolor L.
Iris cristata Ait.
Iris verna L.
Sisyrinchium graminoides Bicknell.
Sisyrinchium augustifolium Mill.

*Orchidaceae*

Achroanthes unifolia (Michx.) Raf.
Leptorchis liliifolia (L.) Kuntze.
Corallorrhiza Corallorrhiza (L.) Kars.
Corallorrhiza odontorhiza (Willd.) Nutt.
Corallorrhiza multiflora Nutt.
Aplectrum spicatum (Walt.) B. S. P.

Tripularia unifolia (Muhl.) B. S. P.
Limodorum tuberosum L.
Pogonia ophioglossoides (L.) Ker.
[1] Pogonia trianthophora (Sw.) B. S. P.
Pogonia divaricata (L.) R. Br.
Arethusa bulbosa L.
Orchis spectabilis L.
Habenaria ciliaris (L.) R. Br.
Habenaria lacera (Michx.) R. Br.
Habenaria cristata (Michx.) R. Br.
Habenaria peramoena Gray.
Habenaria blephariglottis (Willd.) Torr.
Habenaria integra (Nutt.) Spreng.
Habenaria clavellata Spreng.
Gyrostachys cernua (L.) Kuntze.
Gyrostachys gracilis (Bigel.) Kuntze.
Gyrostachys odorata (Nutt.) Kuntze.
Peramium pubescens (Willd.) Mac M.
Cypripedium acaule Ait.
Cypripedium hirsutum Mill.
Cypripedium parviflorum Salisb.

## DICOTYLEDONS

*Salicaceae*

Salix nigra Marsh.
Salix tristis Ait.

*Juglandaceae*

Hicoria alba (L.) Britton
Hicoria glabra (Mill.) Britton.
Hicoria ovata (Mill.) Britton
Juglans nigra L.
Juglans cinerea L.

[1] The illustration of this plant in Britton & Brown's Illustrated Flora, 1st edition does not well represent our plant. The lip of our plant is decidedly three lobed with the lateral lobes connivent above the central lobe, which latter is longer than the others.

Moreover it is certainly crested with a green crest, beginning as two green ridges which coalesce toward the end of the lip. The crest consists of separate, elevated ridges which would seem to come under the definition of "crested" as given in Gray's Glossary.

*Betulaceae*

Carpinus caroliniana Walt.
Corylus americana Walt.
Corylus rostrata Ait.
Betula nigra L.
Betula lenta L.
Betula lutea Michx. f.
Alnus rugosa (Du Roi.) K. Koch.

*Fagaceae.*

Fagus americana Sweet.
Quercus rubra L.
Quercus coccinea Wang.
Quercus velutina Lam.
Quercus digitata (Marsh.) Sudw.
Quercus marylandica Michx.
Quercus imbricaria Michx.
Quercus alba L.
Quercus minor (Marsh.) Sarg.
Quercus Prinus L.
Castanea dentata (Marsh.) Borkh.
Castanea pumila (L.) Mill.

*Urticaceae*

Urticastrum divaricatum (L.) Kuntze.
Boehmeria cylindrica (L.) Willd.

*Santalaceae*

Pyrularia pubera Michx.
Comandra umbellata (L.) Nutt.

*Loranthaceae*

Phoradendron flavescens (Pursh.) Nutt.

*Aristolochiaceae*

Asarum Memmingeri Ashe.

*Polygonaceae*

Rumex acetosella L.
Rumex crispus L.
Polygonum Persicaria L.

Polygonum orientale L.
Polygonum tenue Michx.
Polygonum ramosissimum Michx.
Polygonum sagittatum L.
Polygonum dumetorum L.
Polygonum virginiana L.

*Chenopodiaceae*
Chenopodium album L.

*Amaranthaceae*
Amaranthus hybridus L.

*Phytolaccaceae*
Phytolacca decandra L.

*Caryophyllaceae*
Silene virginica L.
Silene stellata Ait.
Saponaria officinalis L.
Arenaria glabra Michx.
Alsine pubera (Michx.) Britton.
Alsine media L.
Cerastium vulgatum L.
Anychia dichotoma Michx.
Anychia canadensis L.

*Portulacaceae*
Talinum teretifolium Pursh.

*Nymphaeaceae*
Nymphaea advena Soland.

*Ranunculaceae*
Clematis virginiana L.
Anemone quinquefolia L.
Anemone trifolia L.
Anemone virginiana L.
Syndesmon thalictroides (L.) Hoffing.
Thalictrum dioicum L.
Thalictrum clavatum DC.
Thalictrum polygamum Muhl.

Thalictrum macrostylum (Shultt.) Small and Heller. Rare, growing in dry woods.
Thalictrum purpurascens L.
Thalictrum revolutum DC.
Trautvetteria carolinensis (Walt.) Vail.
Ranunculus abortivus L.
Ranunculus recurvatus Poir.
Ranunculus septentrionalis Poir.
Ranunculus hispidus Michx.
Aquilegia canadensis L.
Aconitum uncinatum L.
Aconitum uncinatum var. alpinum. This variety grows on Sugar Loaf Mountain and is perfectly erect, ½ to 2 feet high, with leaves smaller and more deeply and more shapely divided than the common form. In this it approaches *Aconitum noveboracense* Gray.
Xanthorrhiza apiifolia L'Her.
Cimicifuga racemosa (L.) Nutt.

*Magnoliaceae*

Magnolia Fraseri Walt.
Liriodendron Tulipifera L.

*Calycanthaceae*

Butneria florida (L.) Kearney.
Butneria fertilis (Walt.) Kearney.

*Berberidaceae*

Caulophyllum thalictroides Michx. In mountain coves.
Podophyllum peltatum L.

*Lauraceae*

Sassafras Sassafras (L.) Karst.
Benzoin Benzoin (L.) Coulter.

*Papaveraceae*

Capnoides sempervirens (L.) Borck.
Sanguinaria canadensis L.

*Cruciferae*

Arabis canadensis L.
Sisymbrium thalianum (L.) J. Gay.
Bursa Bursa-pastoris (L.) Britton.
Cardamine hirsuta L.
Draba verna L.

*Sarraceniaceae*

Sarracenia purpurea L.
Sarracenia rubra Walt. This plant has a delightful odor of violets not mentioned in books.

*Droseraceae*

Drosera rotundifolia L.

*Saxifragaceae*

Heuchera americana L.
Heuchera hispida Pursh.
Heuchera villosa Michx.
Heuchera pubescens Pursh.
Saxifraga Michauxii Britton.
Hydrangea radiata Walt.

*Hamamelidaceae*

Hamamelis virginica L.
Itea virginica L.

*Platanaceae*

Platanus occidentalis L.

*Rosaceae*

Opulaster opulifolius (L.) Kuntze.
Spiraea salicifolia L.
Spiraea tomentosa L.
Aruncus Aruncus (L.) Karst.
Porteranthus trifoliatus (L.) Britt.
Porteranthus stipulatus (Muhl.) Britt.
Agrimonia striata Michx.
Agrimonia pumila Muhl.
Agrimonia parviflora Soland.
Sanguisorba canadensis L.
Geum virginianum L.

Geum flavum (Porter) Bicknell.
Potentilla monspeliensis L.
Potentilla canadensis L.
Potentilla canadensis var. simplex (Michx.) T.&G.
Fragaria virginiana Duchesne.
Rubus hispidus L.
Rubus trivialis Michx.
Rubus occidentalis L.
Rubus villosus Ait.
Rosa carolina L.
Rosa rubiginosa L.
Rosa pumilis Marsh.
Crataegus uniflora Muench.
Crataegus flava Ait.
Crataegus cordata (Mill.) Ait.
Crataegus Crus-galli L.
Amelanchier canadensis (L.) Medic.
Amelanchier Botryapium (L.) DC.
Malus augustifolia (Ait.) Michx.
Malus coronaria (L.) Nutt.
Aronia arbutifolia (L.) Ell.
Aronia nigra (Walld.) Britt.
Prunus cuneata Raf.
Prunus umbellata Ell.
Prunus serotina Ehrh.

*Leguminosae*

Morongia uncinata (Walld.) Britton.
Cassia nictitans L.
Cassia chamaecrista L.
Cassia marylandica L.
Trifolium agrarium L.
Trifolium pratense L.
Trifolium repens L.
Trifolium procumbens L.
Amorpha fruticosa L.
Amorpha virgata Small.

Robinia pseudacacia L.
Robinia hispida L.
Robinia Boyntonii Ashe.
Robinia nana (Ell.) Sharp.
Cracca virginana L.
Phaseolus polystachyus (L.) B. S. P.
Vicia sativa L.
Vicia caroliniana Walt.
Stylosanthes biflora (L.) B. S. P.
Lespedeza repens (L.) Bart.
Lespedeza procumbens Michx.
Lespedeza Nuttalii Darl.
Lespedeza Stuvei Nutt.
Lespedeza hirta (L.) Ell.
Lespedeza virginica (L.) Britton.
Lespedeza capitata Michx.
Lespedeza striata (Thunb.) H. & A.
Apios Apios (L.) Mac M.
Clitoria mariana L.
Falcata comosa (L.) Kuntze.
Falcata Pitcheri (F. & G.) Kuntze.
Baptisia tinctoria (L.) R. Brown.
Thermopsis caroliniana (Nutt.) M. A. C.
Thermopsis fraxinifolia M. A. C.
Thermopsis mollis (Michx.) M. A. C.
Meibomia nudiflorum (L.) Kuntze.
Meibomia paniculata (L.) Kuntze.
Meibomia paniculata Chapmani Britton.
Meibomia bracteosa (Michx.) Kuntze.
Meibomia Michauxii Vail.
Meibomia laevigata (Nutt.) Kuntze.
Meibomia grandiflora (Walt.) Kuntze.
Meibomia stricta (Pursh) Kuntze.
Meibomia arenicola Vail.
Meibomia obtusa (Muhl.) Vail.
Meibomia Dillenii (Darl.) Kuntze.
Meibomia canescens (L.) Kuntze.

Meibomia rigida (Ell.) Kuntze.
Meibomia rhombifolia (Ell.) Vail.
Galactia volubilis (L.) Britton.

*Linaceae*

Linum medium (Planc) Britton.
Linum striatum Walt.
Linum virginianum L.

*Oxalidaceae*

Oxalis stricta L.
Oxalis cymosa Small.

*Geraniaceae*

Geranium maculatum L.
Geranium carolinianum Muhl.

*Polygalaceae*

Polygala cruciata L.
Polygala Curtisii forma albiflora.
Polygala senega L.
Polygala ambigua Nutt.
Polygala mariana Mill.
Polygala viridescens L.

*Euphorbiaceae*

Euphorbia maculata L.
Euphorbia corollata L.
Acalypha virginica L.
Acalypha gracilens A. Gray.
Crotonopsis linearis Michx.

*Anacardiaceae*

Rhus glabra L.
Rhus copalina L.
Rhus radicans L.
Rhus Toxicodendron L.
Rhus vernix L.

*Aquifoliaceae*

Ilex opaca Ait.
Ilex ambigua Chapm.
Ilex verticillata (L.) Gray.

*Sapindaceae*

Acer saccharinum L.
Acer carolinianum Walt.
Acer rubrum L.

*Balsaminaceae*

Impatiens biflora Walt.
Impatiens aurea Muhl.

*Rhamnaceae*

Ceanothus americanus L.

*Celastraceae*

Euonymus americanus L.
Euonymus obovatus Nutt.

*Vitaceae*

Vitis Labrusca L.
Vitis aestivalis Michx.
Ampelopsis quinquefolia Michx.

*Tiliaceae*

Tilia heterophylla Vent.

*Malvaceae*

Abutilon Abutilon L.

*Hypericaceae*

Hypercium maculatum Walt.
Hypericum canadense L.
Hypericum virgatum. Lam.
Sarothra gentianoides L.
Ascyrum stans Michx.
Ascyrum hypericoides L.

*Cistaceae*

Helianthemum canadense (L.) Michx.
Lechea racemulosa Michx.

*Violaceae*

Viola palmata L.
Viola villosa Walt.
Viola ovata Nutt.
Viola obliqua Hill.

Viola pedata L.
Viola rotundifolia Michx.
Viola blanda Willd.
Viola primulaefolia L.
Viola hastata Michx.
Viola pubescenes Ait.
Viola scabriuscula (T. & G.) Schwein.
Viola canadensis L.
Viola rostrata Pursh. Only found East of the Blue Ridge.
Viola tripartita Ell.

*Passifloraceae*

Passiflora incarnata L.

*Lythraceae*

Parsonsia petiolata (L.) Rusby.

*Melastomaceae*

Rhexia mariana L.
Rhexia virginica L.

*Onagraceae*

Ludvigia alternifolia L.
Ludvigia hirtella Raf.
Epilobium coloratum Muhl.
Kneiffia fruticosa (L.) Raimann.
Kneiffia fruticosa pilosella (Raf.) Britton.
Kneiffia glauca (Michx.) Spach.
Oenothera laciniata Hill.
Onagra biennis (L.) Scop.

*Araliaceae*

Aralia spinosa L.

*Umbellifereae*

Sanicula gregaria Bick.
Sanicula canadensis L.
Eryngium aquaticum L.
Eryngium intergrifolium Walt.
Cicuta maculata L.
Zizia aurea (L.) Koch.

Zizia Bebbii (Coult. & Rose) Britton.
Zizia cordata (Walt.) DC.
Ligusticum canadense (L.) Britton.
Oxypolis rigidus (L.) Britton.
Angelica villosa (Walt.) B. S. P.

*Cornaceae*

Cornus florida L.
Cornus amomum Mill.
Nyssa sylvatica Marsh.

*Ericaceae*

Clethra acuminata Michx.
Chimaphila maculata (L.) Pursh.
Monotropa uniflora L.
Hypopitys Hypopitys (L.) Small.
Monotropsis odorata Ell.
[2] Epigaea repens L.
Gaultheria procumbens L.
Leucothoe Catesbaei (Walt.) A. Gray.
Leucothoe racemosa (L.) A. Gray.
Leucothoe recurva (Buckl.) A. Gray.
Chamaedaphne calyculata (L.) Moench.
Xolisma ligustrina (L.) Britton.
Oxydendrum arboreum (L.) DC.
Kalmia latifolia L.
Kalmia augustifolia L.
Rhodondron maximum L.
Rhodondron catawbiense Michx.
Rhodondron punctatum Andr.
Azalea nudiflora L.
Azalea lutea L.
Azalea arborescens Pursh.
Azalea viscosa L.
Azalea viscosa nitida (Pursh.) Britton.

[2] A form of this plant grows on Wolf mountain near Lake Kanuga which differs from the usual form in having larger and more hairy leaves, being robust and ascending, not lying so flat on the ground and having the flowers slightly different in outline and not clustered, but distributed in a longer inflorescense. It was submitted to Dr. Small, but he regarded it only as a form, and much like specimens he had from South Carolina.

Gaylussacia resinosa (Ait.) T. & G.
Gaylussacia dumosa (Andr.) T. & G.
Vaccinium corymbosum L.
Vaccinium vacillans Kalm.
Vaccinium pallidum Ait.
Vaccinium stamineum L.

*Diapensiaceae*
Galax aphylla L.

*Primulaceae*
Lysimachia quadrifolia L.
Lysimachia terrestris (L.) B. S. P.
Steironema lanceolatum (Walt.) A. Gray.
Steironema ciliatum (L.) Raf.

*Ebenaceae*
Diospyros virginiana L.

*Styracaceae*
Mohrodendron carolinum (L.) Britton.

*Oleaceae*
Fraxinus americanna L.
Chionanthus virginica L.

*Gentianaceae*
Sabbatia angularis (L.) Pursh.
Sabbatia campanulata (L.) Torr.
Gentiana Saponaria L.
Gentiana villosa L.
Gentiana quinquefolia L.
Bartonia virginica (L.) B. S. P.
Obolaria virginica L.

*Apocynaceae*
Apocynum androsaemifolium L.

*Asclepiadaceae*
Asclepias quadrifolia Jacq.
Asclepias obtusifolia Michx.
Asclepias tuberosa L.
Asclepias incarnata L.

Asclepias variegata L.
Asclepias exaltata (L.) Muhl.

*Convolvulaceae*

Quamoclit Quamoclit (L.) Britton.
Ipomoea pandurata (L.) Meyer.
Convolvulus Spithamacus L.
Cuscuta Gronovii Willd.
Cuscuta compacta Juss.

*Polemoniaceae*

Phlox paniculata L.
Phlox glaberrima L.
Phlox amoena Sims.
Phlox divaricata L.

*Verbenaceae*

Verbena urticifolia L.

*Labiatae*

Lycopus virginicus L.
Lycopus sessilifolius A. Gray.
Cunila origanoides (L.) Britt.
Koellia flexuosa (Walt.) Mac M.
Koellia incana (L.) Kuntze.
Koellia montana (Michx.) Kuntze.
Koellia pycnanthemoides (Lavenw) Kuntze.
Koellia clinopodioides (T. & G.) Kuntze.
Collinsonia canadensis L.
Hedeoma pulegioides (L.) Pers.
Glecoma hederacea L.
Salvia lyrata L.
Monarda didyma L.
Monarda punctata L.
Monarda fistulosa L.
Monarda Clinopodia L.
Prunella vulgaris L.
Scutellaria lateriflora L.
Scutellaria incana Muhl.
Scutellaria pilosa Michx.

Scutellaria integrifolia L.
Scutellaria cordifolia Muhl.
Physostegia virginiana (L.) Benth.
Lamium amplexicaule L.
Stachys aspera Michx.
Trichostema dichotomum L.
Trichostema lineare Nutt.

*Solonaceae*

Solanum nigrum L.
Solanum carolinense L.
Datura stramonium L.

*Serophulariaceae*

Verbascum Thapsus L.
Chelone glabra L.
Chelone Lyoni Pursh.
Chelone Cuthbertii Small.
Penstemon hirsutus (L.) Wlld.
Penstemon Penstemon (L.) Wlld.
Linaria Linaria (L.) Karst.
Mimulus ringens L.
Gratiola viscosa Schwein.
Veronica officinalis L.
Veronica serpyllifolia L.
Dasystoma Pedicularia (L.) Benth.
Dasystoma flava (L.) Wood.
Dasystoma virginica (L.) Britton.
Gerardia tenuifolia Vahl.
Gerardia Skinneriana Wood.
Gerardia purpurea L.
Pedicularis canadensis L.
Melampyrum lineare Lam.

*Lentibulariaceae*

Utricularia subulata L.

*Orbobanchaceae*

Thalesia uniflora (L.) Britton.

*Phrymaceae*

Phryma Leptostachya L.

*Plantaginaceae*

Plantago major L.
Plantago lanceolata L.

*Rubiaceae*

Galium triflorum Michx.
Galium tinctorium filifolium Wiegand.
Galium circaezans Michx.
Galium pilosum Ait.
Galium trifidum L.
Galium latifolium Michx.
Houstonia caerulea L.
Houstonia serpyllifolia Michx.
Cephalanthus occidentalis L.
Diodea teres Walt.
Mitchella repens L.

*Caprifoliaceae*

Lonicera sempervirens L.
Lonicera flava Sims.
Viburnum dentatum L.
Viburnum acerifolium L.
Viburnum nudum L.
Viburnum prunifolium L.
Viburnum Lentago. L.
Sambucus canadensis L.

*Campanulaceae*

Campanula aparinoides Pursh.
Campanula divaricata Michx.
Legouzia perfoliata (L.) Britton.

*Lobeliaceae*

Lobelia puberula Michx.
Lobelia Canbyi A. Gray.
Lobelia Nuttallii R. & S.
Lobelia leptostachys A. D. C.
Lobelia inflata L.

Lobelia glandulifera (A. Gray) Small.
Lobelia cardinalis L.
Lobelia amoena Michx.
Lobelia syphilitica L.
Lobelia spicata Lam.

*Compositae*

Vernonia noveboracensis (L.) Willd.
Elephantopus tomentosus L.
Lacinaria scariosa (L.) Hill.
Lacinaria spicata (L.) Kuntze.
Eupatorium aromaticum L.
Eupatorium ageratoides L. f.
Eupatorium perfoliatum L.
Eupatorium sessilifolium L.
Eupatorium album L.
Eupatorium purpureum L.
Eupatorium trifolium L.
Eupatorium serotinum Michx.
Eupatorium semiserratum DC.
Eupatorium incarnatum Walt.
Aster macrophyllus L.
Aster Curtisi T. & G.
Aster patens Ait.
Aster undulatus L.
Aster ericoides pilosus (Willd.) Porter.
Aster dumosus cordifolius (Michx.) T. & G.
Aster puniceus L.
Aster tenuifolius L.
Aster lateriflorus (L.) Britton.
Aster concolor L.
Aster Tradescanti L.
Aster acuminatus Michx.
Aster divaricatus L.
Aster junceus Ait.
Doellingeria unbellata (Mill.) Nees.
Doellingeria infirma (Michx.) Greene.

Ionactis linariifolius (L.) Green.
Seriococarpus asteroides (L.) B. S. P.
Erigeron pulchellus Michx.
Erigeron annuus (L.) Pers.
Leptilon canadense (L.) Britton.
Solidago patula Muhl.
Solidago hispida Muhl.
Solidago Boottii Hook.
Solidago erecta Pursh.
Solidago odora Ait.
Solidago serotina Ait.
Solidago rugosa Mill.
Solidago monticola T. & G.
Solidago lancifolia T. & G.
Solidago Buckleyi T. & G.
Solidago canadensis L.
Solidago puberula Nutt.
Solidago nemoralis Ait.
Solidago Curtisii T. & G.
Brachychaeta sphacelata (Raf.) Britt. Sugarloaf Mountain.
Chrysopsis mariana L.
Chrysopsis graminofolia (Michx.) Nutt.
Antennaria plantaginifolia (L.) Richards.
Gnaphalium obtusifolium L.
Silphium compositum Michx.
Parthenium integrifolium L.
Ambrosia artemisaefolia L.
Xanthium strumarium L.
Rudbeckia laciniata L.
Rudbeckia hirta L.
Rudbeckia spathulata Michx.
Rudbeckia fulgida Ait.
Helianthus atrorubens L.
Helianthus strumosus L.
Helianthus microcephalus T. & G.
Verbesina occidentalis (L.) Walt.

Coreopsis major Walt.
Coreopsis pubescens Ell.
Coreopsis crassifolia Ait.
Bidens trichosperma (Michx.) Britt.
Bidens trichosperma var. tenuiloba (A. Gray) Britton.

Bidens bipinnata L.
Bidens bipinnata var. minor. Very delicate, small 10 cm. high, in dense shade on rocks.

Bidens frondosa L.
Bidens connata Muhl.
Galinsoga parviflora Cav. Introduced, a nuisance in gardens.

Helenium autumnale L.
Achillea millefolium L.
Anthemis cotula L.
Chrysanthemum Leucanthemum L.
Senecio aureus L.
Senecio Smallii Britton.
Senecio Balsamitae Muhl.
Senecio millefolium T. & G.
Senecio Memmingeri Britton.
Erechtites hieracifolia (L.) Raf.
Mesadenia atriplicifolia (L.) Raf.
Synosma suaveolens (L.) Raf.
Carduus muticus (Michx.) Pers.
Carduus altissimus L.
Adopogon carolinianum (Walt.) Britton.
Hieracium paniculatum L.
Hieracium venosum L.
Hieracium Gronovii L.
Hieracium scabrum Michx.
Nabalus altissimus (L.) Hook.
Nabalus serpentarius (Pursh) Hook.
Nabalus albus (L.) Hook.

Nabalus integrifolius Cap.
Nabalus trifoliolatus Cap.
Lactuca canadensis L.
Sonchus oleraceus L.
Sonchus asper (L.) All.

# THE STABILITY OF RESIN ACIDS AT SLIGHTLY ELEVATED TEMPERATURES—A CORRECTION *

BY CHAS. H. HERTY AND H. L. COX

Schwalbe,[1] noting the evolution of carbon dioxide when rosin was heated to 140° C. in air freed from carbon dioxide, interpreted this result as the breaking down of the carboxyl groups of the acids contained in the rosin.

Herty and Dickson [2] showed that the carbon dioxide obtained by Schwalbe was due to one or more of the following factors: traces of spirits of turpentine in the rosin, moisture, oxygen of the air conducted through the heating flask and oxygen absorbed by the rosin previous to the experiment. Rosin, prepared from fresh oleoresin, freed completely from spirits of turpentine during distillation, and heated in a current of dry nitrogen, showed no signs of decomposition at 140°, even after seven hours' heating at this temperature.

But they further stated that if the resin acids were prepared cold and freed from the other constituents of the fresh oleoresin, such acids heated in dry nitrogen melted at 65°-70° C. and immediately evolved carbon dioxide in quantity. No explanation was offered of this seeming paradox, the results, however, indicating a probable decomposition of some of the acid constituents of the oleoresin during its separation by distillation, in the woods, into rosin and spirits of turpentine.

Later, in seeking an explanation, two possibilities suggested themselves: *First,* that during the preparation of the acids some oxygen might have been absorbed from the air, in spite of the precautions taken; *second,* that the drying of the acids in a desiccator over phosphorus pentoxide may have been imperfect. This last idea was suggested during the course of another investigation in this laboratory, in which great difficulty was experienced in drying perfectly resin acids precipitated

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[1] *Zeit. angew, Chem.,* **18**, 1825.

[2] THIS JOURNAL, **1**, 68.

from water solutions of their potassium salts by acidifying with hydrochloric acid.

To test these ideas, a perfectly fresh specimen of the oleoresin of *Pinus Heterophylla* (Cuban or slash pine) was obtained from Florida. Five grams of this specimen were dissolved in 50 cc. of ether, the solution filtered and the potassium salts of the acids immediately precipitated by slowly adding 10 cc. of a very concentrated water solution of potassium hydroxide, approximately 15 normal, a salting-out process. This precipitate, freed as far as possible from the potassium hydroxide solution by draining, was thoroughly mixed with glass wool to make the mass more permeable to the extractive, and extracted with ether one hundred hours in a Soxhlet extractor until no further traces of spirits of turpentine or resene could be detected in the fresh extract. The extracted mass was treated with cold water and the solution of the potassium salts filtered from the glass wool. The free acids were precipitated by slow addition of dilute hydrochloric acid, just to acidity, filtered upon a Buchner funnel, washed with water until free from chlorides, and rapidly dried as far as possible with the suction pump. The partly dried acids were dissolved in ether and the removal of water completed by addition of freshly ignited sodium sulfate. This solution was rapidly filtered into the heating flask in which the experiment was to be conducted.

This flask had been previously filled with nitrogen obtained by drawing air successively through a water solution of ammonia; over heated copper; through dilute sulfuric acid; two wash bottles containing alkaline pyrogallic acid solution; concentrated sulfuric acid and two drying tubes—one containing calcium chloride and soda lime, the other phosphorus pentoxide mixed with pumice. The heating flask, surrounded by a bath of cottonseed oil in a beaker, contained a thermometer, and its outlet tube, during the heating experiment, dipped below the surface of freshly filtered barium hydroxide solution in the precipitating flask. A tube of soda-lime was placed between the precipitating flask and the aspirator.

The ether solution of the resin acids was evaporated to

dryness in the heating flask in a current of dry nitrogen under reduced pressure, barium hydroxide solution was then filtered into the precipitating flask and the temperature of the heating flask slowly raised, nitrogen being drawn through the flask throughout the experiment.

The acids melted at about 73°C., but no gas evolution could be detected in the melted mass, even while the temperature was being raised to 140° C. and so maintained for an hour, nor was there the slightest precipitation of barium carbonate in the precipitating flask. It is evident, therefore, that these resin acids, if protected from oxygen and thoroughly freed from water, are perfectly stable at 140° C.

CHAPEL HILL, N. C.

# ISOPRENE FROM COMMERCIAL TURPENTINES *

BY CHAS. H. HERTY AND J. O. GRAHAM

In connection with the studies of rubber made by polymerization of isoprene, Harries and Gottlob [1] described a method for the preparation of isoprene from spirits of turpentine by means of the "isoprene lamp." In this method the spirits of turpentine is boiled in a flask, in which, just below the neck, is suspended an electrically heated platinum wire coiled somewhat like the filament of a tantalum incandescent bulb. A part of the vapors are decomposed as they pass upward across the heated wire. The flask is attached to an upright condenser maintained at a temperature of 50° C., for condensing the unchanged vapors of spirits of turpentine. The upright condenser is connected with an inclined condenser fed with tap water and this in turn is connected with a receiver surrounded by a freezing mixture. The crude product collected in this receiver is fractionated and the isoprene collected as the fraction boiling between 35° and 37° C.

With this apparatus, Harries and Gottlob obtained a yield of only 1 per cent of isoprene from commercial pinene as against 30 to 50 per cent from commercial limonene. They, therefore, concluded that the yield of isoprene from spirits of turpentine is due chiefly to the presence of dipentene (limonene).

In view of the general interest in the production of rubber from isoprene, it seemed desirable to extend these studies to commercial products closely related to spirits of turpentine and to test further the point mentioned above as to the origin of the isoprene from spirits of turpentine, accordingly, studies have been made using commercial spirits of turpentine, fractions of the same, pine oil, the volatile oil of *Pinus serotina* (pond pine) and refined spruce pine teurpentine.

The apparatus used closely resembled that of Harries and Gottlob, short-circuiting of the sections of red hot platinum wire being prevented by winding the wire on a pipe stem triangular

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[1] *Ann.*, **383**, 228.

prism. A constant current of 2.25 amperes maintained an even temperature of the wires at a red glow. The flask containing the turpentine was heated by means of a bath of cottonseed oil containing a thermometer. The receiving vessel in the freezing mixture, salt and ice, was a small sulfurous acid condenser. The crude products were refined by distillation through a Hempel column filled with glass beads. The yield of pure isoprene in each of the experiments which follow represents the fraction collected between 35° and 37° C.

### SPIRITS OF TURPENTINE

200 cc. of spirits of turpentine were boiled in the isoprene lamp until condensation ceased in the inclined condenser. At two-hour intervals the crude product was removed from the receiver and fractionated. Following this experiment, similar experiments were conducted with 200 cc. fractions of spirits of turpentine obtained by fractionation by means of a Young's still head. The first fraction was collected between 155° and 156° C., the pinene fraction; the second, between 169° and 175° C.; the third fraction from 175° C. up. These two last fractions should include the dipentene content of the original spirits of turpentine.

The heating of the two last fractions was continued only two hours, as after that time no further condensation could be observed in the inclined condenser.

The results of the three experiments are shown in Table I:

TABLE I

| Substance used | Time of heating Hrs. | Temperature of oil bath | Volume of distillate: Crude Cc. | Volume of distillate: Refined Cc. | Per cent of isoprene | Volume of residue in heat'g flask Cc. |
|---|---|---|---|---|---|---|
| | 2 | 175° | 17 | 6.5 | 3.25 | ... |
| Spirits of turpentine..... | 2 | 175° | 12 | 3.5 | 1.75 | ... |
| | 2 | 185° | 8 | 1.0 | 0.50 | 103 |
| Totals..... | 6 | .... | 37 | 11.0 | 5.50 | 103 |
| Fraction 155°—156°..... | | | | | | |
| | 2 | 175° | 10 | 6 | 3.00 | ... |
| | 2 | 175° | 7 | 5 | 2.50 | ... |
| | 2 | 175° | 6 | 4 | 2.00 | ... |
| | 2 | 175° | 4 | 1 | 0.50 | ... |
| Totals..... | 8 | .... | 27 | 16 | 8.00 | 50 |
| Fraction 169°—175° ..... | 2 | 180° | 6.5 | 1 | 0.50 | 192 |
| Fraction 175°+ ..... | 2 | 185° | 3.25 | 0 | 0.00 | 195 |

From the direct proof thus obtained it is evident that the yield of isoprene from spirits of turpentine is due to pinene, rather than to dipentene as claimed by Harries and Gottlob.

### THE VOLATILE OIL OF PINUS SEROTINA

This substance has been studied by Herty and Dickson [2] and was found to be particularly rich in limonene. Since Harries and Gottlob obtained 30 to 50 per cent of isoprene from commercial limonene with the isoprene lamp, it seemed desirable to study this volatile oil and compare its yield with that from ordinary spirits of turpentine.

In preparing the material from the oleoresin the difficulties formerly met with in distillation by a current of superheated steam were easily overcome by heating the oleoresin at a pressure of one millimeter, the volatile oil readily passing off without any tendency to froth in the flask and with largely decreased opportunity for polymerization during distillation. Table II gives the results with the isoprene lamp.

TABLE II

| Substance used | Time of heating Hrs. | Temperature of oil bath | Volume of distillate: Crude Cc. | Volume of distillate: Refined Cc. | Per cent of isoprene | Volume of residue in heat'g flask Cc. |
|---|---|---|---|---|---|---|
| | 2.0 | 175° | 6.50 | 5.0 | 2.5 | ... |
| 200 cc. of volatile oil of *Pinus* | 2.0 | 175° | 4.75 | 3.0 | 1.5 | ... |
| *serotina* | 2.5 | 185° | 11.00 | 8.0 | 4.0 | ... |
| | 2.5 | 185° | 11.00 | 8.0 | 4.0 | 25.0 |
| Totals | 9.0 | .... | 33.25 | 24.0 | 12.0 | 25.0 |

No further condensate could be obtained by continued heating of the residue. As was to be expected the yield of isoprene from this volatile oil, rich in limonene, shows a largely increased yield, practically doubled, as compared with ordinary spirits of turpentine.

[2] *J. Am. Chem. Soc.*, **30**, 872.

PINE OIL

When resinous pine wood is finely divided and treated with steam a crude oil distils off which on fractionation yields wood spirits of turpentine and pine oil. Teeple [3] has found that pine oil consists chiefly of α-terpineol. The specimen used in this work showed at 15° C. a specific gravity of 0.9403 and an index of refraction of 1.4901. The results with the isoprene lamp are given in Table III.

TABLE III

| Substance used | Time of heating Hrs. | Temperature of oil bath | Volume of distillate: Crude Cc. | Volume of distillate: Refined Cc. | Per cent of isoprene | Volume of residue Cc. |
|---|---|---|---|---|---|---|
| | 2 | 210° | 15 | 4 | 2.0 | ... |
| 200 cc. of pine oil..... | 2 | 210° | 10 | 3 | 1.5 | ... |
| | 2 | 210° | 7 | 1 | 0.5 | 125 |
| Totals..... | 6 | .... | 32 | 8 | 4.0 | 125 |

REFINED SPRUCE PINE TURPENTINE

This substance, consisting chiefly of cymene, is collected as a by-product in blowing off the digesters in the manufacture of wood pulp from spruce pine. The specimen was furnished by the A. D. Little Laboratory of Boston. It showed at 15° C. a specific gravity of 0.8639 and an index of refraction of 1.4916; 80 per cent distilled between 171.3° and 174.9°C. 200 cc. of this substance were boiled three hours in the isoprene lamp but no crude distillate could be observed.

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[3] *J. Am. Chem. Soc.*, **30**, 413.